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(54) **ADDITION OF MAGNETIC MOIETIES IN FLUID BED HYDROCARBON PROCESSING.**

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Description

In fluid bed particulate processing of hydrocarbon feedstocks, it is the practice to continuously add fresh particulate regularly, usually daily, and to withdraw equilibrium particulates prior to addition of fresh particulates. This provides room for the incoming fresh material.

Because of this procedure, which results in immediate complete mixing, particulates both fresh in performance and low in contaminants (usually nickel, vanadium, iron, copper, and sodium) are unavoidably withdrawn together with particulates which have been in the unit for varying times as long as two or three months or longer and have aged and drastically dropped in performance, while simultaneously accumulating deleterious metal contaminant. The industry has long felt a need to have a means by which old catalyst can be selectively removed without entrainment of fresh catalyst.

The techniques of USSN 07/332,079 filed April 3, 1989 (attorney docket 6324AUS) are useful with the present invention.

A manual search in the U.S. Patent Office, Class 55, subclass 3; Class 208, subclasses 52CT, 113, 119, 120, 121, 124, 137, 139, 140, 152, 251R, and 253; Class 209, subclasses 8, 38, 39, and 40; and Class 502, subclasses 5, 20, 21, 38, 515, 516, and 518 found principally the following references:

U.S. 4,359,379 and 4,482,450 to Ushio (assigned Nippon Oil Company), both disclosed catalytic cracking and hydrotreating processes for carbo-metallic feedstocks by depositing (adding) nickel, vanadium, iron and/or copper (originally contained in the heavy oil), and then separating the old catalyst utilizing a high gradient magnetic separator (HGMS). However the magnetization is derived from the metals contained in the starting oil.

U.S. 2,348,418 (col. 2) to Roesch (Standard Oil, Indiana) regenerates catalyst by adding a magnetic substance, such as iron or nickel to the catalyst before the catalyst is introduced into a magnetic separator.

U.S. 4,292,171 and 4,294,688 both to Mayer (assigned Exxon) show catalytic reforming processes which utilize the addition of magnetizable particles to enhance catalyst separation via the use of magnetically stabilized fluidized beds.

U.S. 4,406,773 to Hettinger (assigned Ashland Oil) discloses magnetic separation of high activity catalyst from low activity catalyst.

U.S. 4,280,896 to Bearden passivates catalyst used to crack hydrocarbon feedstocks wherein nickel, vanadium and/or iron are deposited on the catalyst, but does not mention use of magnetic separation.

However, none of the above patents deliberately adds magnetically active substances such as iron at a constant rate over a period of time so that the magnetically active substance builds up on the catalyst in proportion to the age of the catalyst (the length of time the catalyst has been in the hydrocarbon conversion system). This addition of magnetic "hooks" which facilitate separation of old (lower activity) from new (recently added higher activity) catalyst is a novel feature of the present invention.

U.S. 4,541,920 to Seiver (Exxon) utilizes particles containing a non-ferromagnetic component and a catalytically active component composited with a ferromagnetic component so that the particles can be lined up in a magnetic field.

If a harmless magnetic substance could be continuously added to these particulates, so that it accumulates at the same rate, as for example, nickel and vanadium, it could be used to efficiently magnetically separate old particulates (those added to the system sometime back) from new (those recently added to the system, thus not heavily contaminated with metals, and therefore valuable for recycle).

This invention teaches that intentional and continuous addition of iron can be used to facilitate separation of old catalyst from new.

Our work has shown that iron contamination of reduced crude cracking catalysts and even FCC catalysts is a recurring catalytic cracking experience and this contamination has enabled us to demonstrate that iron is involved in effecting magnetic separation of used catalysts. In fact, it appears to be the major element affecting magnetic separation of old (metal contaminated) catalyst from new catalyst.

In the earlier years of fluid bed catalytic cracking, iron was considered a mild poison, especially in the presence of high sulfur, and was rated equivalent to 1/7 as deleterious as nickel. (Nickel Equivalents was expressed as equal to: $\text{Ni ppm} + \text{V ppm}/4.8 + \text{Fe ppm}/7.1 + \text{Cu ppm}/1.23$), and as it related to causing an increase in coke and gas (hydrogen make), lower gasoline yield, and lower catalyst activity.

Today, however, in cracking reduced crude containing high Conradson Carbon and high metals with state-of-the-art techniques, e.g. lift gas contacting, highly active zeolite promoted catalysts, riser reactors, (progressive flow), the vented riser and an extremely short (one to five second) residence time in the reactor, it appears that iron is not nearly as harmful as previously experienced. This is shown in Figures 4-6.

The invention comprises continuously adding to the feedstock or the particulate directly a given amount of iron in the range of up two to three times, and possibly more, the level of nickel and vanadium in the feedstock, and added continuously as either an organic compound such as ferrocene, or porphyrin or a water

soluble salt, such as for example, ferrous acetate, ferric formate and ferrous or ferric sulfate or by sublimation, such as Fe C_{13} ; Iron sulfate is used for water treatment and is very inexpensive, being a waste product from titanium dioxide manufacture. Other compounds of iron, either organic, water soluble or oil soluble, may be added. Particularly preferred compounds are iron carbonyl, or the dicyclopentadienyl derivative of iron, such as ferrocene.

The invention is useful for prolonging the life and reducing the cost of sorbents and/or catalyst for hydrocarbon conversion.

Figure 1 is a theoretical example of one metal (nickel) distribution on these particulates as a result of constant addition of fresh particulates, and withdrawal of equilibrium particles. Those portions of the particulates, highest in metal content, have generally been in the unit for the longest period of time.

Figure 2 is a schematic of a hydrocarbon cracking system having a magnetic separation system according to the invention.

Figure 3 is a depiction of a composition of matter comprising catalyst and/or sorbent particles having higher and lower magnetic properties, produced according to the invention.

Figure 4 is a computer-generated plot of coke weight percent versus iron on regenerated catalyst for a major hydrocarbon conversion unit cracking reduced crude and other residual oils, showing that as iron increases, it decreases, or at least does not increase, the coke-make, contrary to the conventional wisdom of the past.

Figure 5 is a computer-generated plot of selectivity in volume percent versus iron on regenerated catalyst for a major hydrocarbon conversion unit cracking reduced crude and other residual oils, showing that increased iron activity does not decrease, the selectivity, contrary to the conventional wisdom of the past.

Figure 6 is a computer-generated plot of hydrogen weight percent versus iron on regenerated catalyst for a major hydrocarbon conversion unit cracking reduced crude and other residual oils, showing that iron decreases, or at least does not increase, the hydrogen production, contrary to the conventional wisdom of the past.

Figure 7 is a plot showing the rare earth roller magnetic separation of a commercial sorbent used in a major metal removal system commercial unit according to the invention. Note that the more magnetic fractions do contain higher amounts of vanadium, nickel and iron.

Figure 8 is a plot showing incremental magnetic susceptibility in electromagnetic units plotted as a direct relationship against incremental iron, plus nickel.

Catalyst/Sorbent:

The invention is useful for a variety of catalysts, sorbents, and even mixtures of catalyst and sorbent. Typical catalysts are those used for cracking of heavy oils, e.g. 2607B by Engelhard Corporation, DZ-40 by W. R. Grace, FOC-90 by Filtrol Corporation, etc. Some catalysts will contain iron or rare earths or other magnetically active materials when they are made. This magnetism can be treated as "background" and the separation can be affected by the fact that the catalyst will become even more magnetic as additional magnetically active ions or elements are deposited on it over time. Nickel, which is deposited deleteriously on the catalyst or sorbent from residual oil feeds, is itself magnetic as shown in Figure 7. Since nickel will be deposited in proportion to time, this additionally assists in removing the more spent catalyst which has been in the conversion system for the longer time.

Preferred catalyst has a nickel equivalent metals content excluding iron of 100 ppm or greater, more preferably 500 ppm or greater, and most preferably 1,000 ppm or greater.

Feed:

Feeds used with the present invention can be any oil suitable for cracking in the presence of any catalyst which loses activity over time. Preferred usage is with any sort of metal-containing feed because it is these feeds which tend to gradually coat the catalyst with metal rendering it less active over a period of time. The same effect holds true for the sorbents used in processes such as the Art[®] metal removal system taught, for example, in U.S. Patents 4,263,128, 4,243,514 and 4,256,567.

Feeds can be those variously called residual oils, topped crudes, extremely high carbo-metallic crudes such as Myan, and most preferably, reduced crudes. Any hydrocarbon feed which contains metals can be used with the invention. The most common contaminating metals are nickel, vanadium, and iron (which is often itself found in residual oils).

Preferred for the invention are feedstocks having Conradson carbon numbers greater than 0.1, more preferably greater than 1, and most preferably greater than 2, and having API gravity between about 5 and 50, more preferably 10 and 40, and most preferably between 15 and 30.

Apparatus:

The apparatus used with the present invention can be the High Gradient Magnetic Separation (HGMS) system described in U.S. 4,406,773, the superconductivity magnetic manufactured by Eriez, and most preferably the rare earth roller magnet described in co-pending patent application USSN 07/332,079 (attorney docket 6324AUS). Several manufacturers including Sala Magnetics and their successors, and Eriez, Inc., and their standard commercial models can be used. The carousel model of Sala Magnetics is especially effective because it is in essence a batch method in which individual portions of catalyst are successively subjected to magnetic fields for separation.

Typical commercial types include the High Gradient Cyclic Magnetic Separator (HGCMS), such as produced by Eriez Magnetics, or a Continuous Carousel Magnetic Separator manufactured by Sala Magnetics, Inc., both of which are capable of achieving 20,000 Gauss magnetic gradient. It may also consist of a Superconductor Cyclic Magnetic Separator produced by Eriez and which is capable of cyclic operation to 50,000 Gauss. Alternate means of separation are the so-called Rare Earth Roller Magnetic Separator (RERMS) and Ferrite Roller Magnetic Separator as manufactured by Eriez Magnetics.

The magnetic field is preferably in the range of about 5,000 to 50,000 gauss, preferably in a super conductor high gradient electromagnetic separator (SCHGMS), and even more preferably in the range of 10,000 to 30,000 gauss.

Magnetically Active Moieties (MAM):

The most preferred magnetically active moiety is iron and its compounds and manganese and chromium and their compounds and/or combinations of all three are also preferred. But any non-deleterious element or compound moiety or combination of more than one moiety from the 57 edition of the Handbook of Chemistry and Physics, pages E122 through E127, preferably having at least about +500, more preferably having at least about +1000, and most preferably having a magnetic susceptibility of at least about $+3500 \times 10^{-6}$ cgs per one gram formula (or atomic) weight at or about 293°K, capable of deposition on catalyst or sorbent over a period of time and readily and usually, although not necessarily, converted to such as, for example, an oxide or sulfide, sulfate or sulfite, or in any other form as, for example, an ion, a surface reactive or inactive specie, or complex oxide as, for example, a spinel or complexed with a zeolite, or the formation or reaction with one or more other magnetically reactive species or a ternary magnetic compound possessing the above magnetic susceptibility properties after deposition on the catalyst (by reduction said additive may also be converted to the metal) can be used with the invention. The preferred forms are inorganic compounds of iron or the other MAM's or organic compounds of iron or the other MAM's. The iron or other MAM may be added as a water soluble compound which is emulsified in oil and added as an additive, or may be added as an oil soluble compound direct in the feed or injected elsewhere in the system, or may be added as a solution or slurry in an organic or other solvent. Preferably the MAM is added so as to deposit in the range of about 0.1 to 10 parts per million, more preferably 0.5 to 2, of iron, (or its equivalent with a particular MAM) for each part of nickel equivalents of metal which are deposited on the catalyst.

Preferred MAM's are ferrous sulfate, and ferric sulfate and any water soluble salts.

The MAM should not, of course, be substantially deleterious to the cracking process (e.g. react with catalyst acid sites) or become magnetically inactive at 293°K after exposure at the temperature e.g. 482.2°C (900°F) or more used in the cracking process.

Addition of MAMs:

The MAMs may be added continuously at a rate in proportion to the average deposition of metals occurring with a particular feed and system being utilized, or may be added intermittently in a similar rate but with injections of MAM being made periodically.

Referring to the Figures, Figure 1 shows the metal distribution on the particulates indicating that those portions of the particulates which are highest in metal content have generally been in the unit for the longest period of time and have lost much of their catalytic or sorbent ability. Selective removal of these, of course, increases the activity of the remaining catalyst and/or sorbent and this is a major object of the present invention.

Figure 2 shows a simplified schematic diagram of a typical riser conversion system in which a reduced crude flows into the riser at injection point 11 and/or 12 after having been injected with a portion of ferric sulfate from tank 13. The flow of ferric sulfate is controlled by valve 14 so that the iron will be 1-5 ppm times the nickel equivalent ppm deposited on the catalyst circulating in the system. Regenerated catalyst flows through line

15 into riser 16 where it meets the feed 11 which contains about one ppm vanadium, one ppm nickel, and one ppm iron for a total metals content of 1.3 nickel equivalents. The catalyst and feed flow in plug-flow, taking about 1.5 seconds to reach separator 17 where the cracked vaporous products 18 are separated from the catalyst now contaminated with vanadium, nickel and iron for a total nickel equivalents in the equilibrium catalyst of about 1000 ppm nickel equivalents. The spent catalyst 19 flows into the regenerator 20 where it is regenerated with air 21 which burns off the coke. Hot regenerated catalyst flows through conduit 15 into separator 23 in which valve 24 is set to remove about 25 percent by weight of the catalyst flowing through conduit 22. The remaining catalyst returns to the riser for contact with further feed. The catalyst is separated out where it flows through cooler 25 and onto belt then past magnetic roller 27 which separates the more magnetic portions from less magnetic portions into four separate portions each more magnetic than the next (28, 29, 30, 31 are each successively less magnetic). The number of portions returned to the catalyst make-up injection point 32 to be mixed with fresh make-up catalyst and recycled through the system, is dependent on the particular operating characteristics of the system with the particular feed and catalyst being employed. Generally the most magnetic 80%, more preferably 50% and most preferably 30 or lower weight percent of the catalyst will be discarded and the remainder recycled back through catalyst make-up inlet 32. The MAT activity, as measured by the usual standard tests, indicates that the more magnetic portion which is discarded has a MAT activity which is substantially lower and a metals content which is substantially higher than the other portion, which is recycled. Discarding the more magnetic portion raises the activity of the total equilibrium catalyst charge in the system and substantially reduces the amount of make-up catalyst required to be added periodically.

Figure 3 shows a section view of a portion of the riser 16 showing magnetic particles (solid black), less magnetic particles (white circles), and vapors (indicated by wavy vertical lines) moving in plug flow up the riser. The particles may be sorbent or catalyst or both intermixed. The average metal on catalyst of the non-magnetic particles is usually 50-90% of the average metal content of the magnetic particles and preferably 60 to 85%.

Referring to Figures 4-6, these show that the addition of iron, conventionally thought to be highly deleterious, has little effect on coke-make gasoline selectivity, and hydrogen-make (gasing), respectively.

Figure 7 shows that the more magnetic portions discarded from the system shown in Figure 2 are high in vanadium and in iron, and somewhat higher in nickel. It is an important feature of the invention that, contrary to the mathematical expression for nickel equivalents which is conventionally employed, vanadium has been found to be even more deleterious than nickel, and its removal from the system substantially enhances the catalyst life and reduces the need for make-up catalyst.

35 Temperature:

Though not narrowly critical, temperature can be used to enhance the process because magnetic susceptibility increases as temperature decreases, with most materials. Preferred temperature ranges are -128.4° to 204.4°C (-200°F to +400°F), more preferably 37.8° to 204.4°C (100°F to 400°F), and most preferably -45.6° to 121.1°C (-50°F to +250°F).

Magnetic Split and Recycle:

With most crudes and catalyst it is preferable to discard from about 1-30, more preferably 3-25, and most preferably 5-15 wt. % of the regenerated catalyst to the magnetic separator. The wt. % sorbent rejected by the magnetic separator is preferably from about 5-50, more preferably about 10-35, and most preferably 15-30% by weight. Economics, desired MAT activity and other factors will affect the optimum split. Discarded catalyst may be processed for metal recovery where economical. Remaining catalyst and sorbent is preferably recycled to the same or another conversion system.

50 Example 1

Referring to Figure 2, reduced crude representing the bottoms derived from distilling off a portion of crude oil 10 enters the riser reactor at 11 after mixing with a metal additive 14 from tank 13. In the riser the reduced crude contacts regenerated catalyst returning from the regenerator line 15 and travels up the riser 16 cracking the reduced crude and generating product 18 and spent catalyst 17 which is contaminated with coke and metals from the reduced crude. The spent catalyst 17 enters the regenerator 20 via line 19 and is oxidized with air 21 to burn off coke and thereby regenerate the catalyst for return to the riser 16. About 8% of the regenerated catalyst is diverted through line 24 to catalyst cooler 25 and to feed to magnetic separator 26, where it falls

onto belt 27, moves past roller, a high intensity rare earth-containing permanent magnetic roller which splits the catalyst into two or more portions 28 to 31. The more magnetic (more metal-contaminated) portions, e.g. 28, and/or 28 & 29 are rejected for chemical reclaiming, metals recovery, or disposal. The less magnetic (less metal-contaminated) portions 30 and 31 travel through line 33 back to the regenerator 20.

Table I shows an analysis and is a typical example of an equilibrium catalyst withdrawn from a fluid bed operation on a high metal containing reduced crude.

TABLE 1
ANALYSIS OF A TYPICAL EQUILIBRIUM REDUCED CRUDE
CATALYST WITH HIGH IRON CONTAMINATION

Iron	1.12 wt. %
Nickel	0.19 wt. %
Vanadium	0.41 wt. %

Example 2

Table 2 shows results from a residual processing run in which the iron level was 6900 ppm on spent equilibrium conversion (RCC process) catalyst processing reduced crude. The results of magnetic separation on a Rare Earth Roller Magnetic Separator (RERMS) are shown in Table 2.

TABLE 2
RCCSM - Spent Catalyst

	Untreated Sample	Magnetically		Separated		Product
		NMag	Mid	Mid	Mid	Mag
Yield, Wt. %	-	24.6	21.3	18.7	17.4	18.0
Vanadium, Wt. %	0.37	0.31	0.34	0.36	0.39	0.46
Nickel, Wt. %	0.12	0.10	0.12	0.13	0.15	0.20
Iron, Wt. %	0.69	0.64	0.67	0.70	0.72	0.87
Carbon, Wt. %	1.06	1.26	1.14	1.04	0.95	0.87
Surface Area, m ² /g	84	88	85	80	76	71
Ratio V/Fe	0.54	0.48	0.51	0.51	0.54	0.53
Ratio V/Ni	3.1	3.1	2.8	2.8	2.6	2.3

In this example iron concentration varies from 6400 ppm at the non-magnetic low metal level to 8700 ppm at the highest level, for an increase of 2300 ppm, while nickel increases from 1200 ppm to 2000 ppm (an increase of 800 ppm). Thus, iron beneficiation is 2.9 times as great as Ni beneficiation. Obviously, beneficiation (separation) is, in a major way, dependent on the magnetic properties of the iron content.

Example 3

Table 3 shows results from essentially the same catalyst as example 2 after being regenerated under commercial operating conditions, wherein catalyst which contains 7100 ppm iron is subjected to magnetic separation. The separation shows an increase from 5800 ppm iron in the non-magnetic portion to 8800 ppm iron in the high magnetic portion, an iron beneficiation of 3000 ppm. Nickel, on the other hand, present at 1400 ppm in the untreated sample, is 800 ppm in the non-magnetic portion and 1900 ppm in the magnetic portion, for a nickel beneficiation of 1100 ppm. Again there is an Fe/Ni beneficiation ratio of 2.7, showing again the effectiveness of iron in facilitating separation.

TABLE 3
RCCSM - Regenerated Catalyst

	Untreated Sample	NMag 2X1	Mid 2X2	Mid 2X3	Mid 2X4	Mag 2X5
Yield, Wt. %	-	11.7	17.9	42.1	11.6	16.7
Vanadium, Wt. %	0.36	0.26	0.34	0.35	0.40	0.44
Nickel, Wt. %	0.14	0.08	0.13	0.12	0.16	0.19
Iron, Wt. %	0.71	0.58	0.67	0.68	0.76	0.88
Carbon, Wt. %	0.05	0.08	0.05	0.05	0.05	0.05
Surface Area, m ² /g	97	113	94	92	89	81
Ratio V/Fe	0.51	0.45	0.51	0.51	0.53	0.50
Ratio V/Ni	2.6	3.3	2.6	2.9	2.5	2.3

Example 4

Table 4 shows results from a run on an Engelhard ARTCAT^R sorbent from the (ART^R) process. The ART process is a process developed for asphalt and metal removal from reduced crude in a fluid bed contacting operation (See U. S. Patents 4,263,128, 4,243,514 and 4,256,567). Here the iron level at the low magnetic end is 5700 ppm for an ARTCAT^R sorbent containing 8200 ppm iron, while the high magnetic end contained iron at 12200 ppm for an iron beneficiation of 6500 ppm. Nickel, with a 3200 ppm level in equilibrium material, increases from 2100 on the low magnetic fraction to 4000 ppm in the high magnetic side, showing a nickel beneficiation of 1900 ppm, compared with iron with an increase of 6500 ppm. Here again, the ratio of Fe/Ni beneficiation is 3.4. Clearly, beneficiation is much more readily achieved due to iron content than nickel content.

TABLE 4

MRS Sorbent

	Untreated Sample	NMag	Mid	Mid	Mid	Mid	Mag
Yield, Wt. %	-	16.6	16.6	16.6	16.6	16.6	16.6
Vanadium, Wt. %	1.07	0.88	0.90	1.17	1.49	1.56	1.52
Nickel, Wt. %	0.32	0.27	0.31	0.38	0.35	0.39	0.44
Iron, Wt. %	0.82	0.70	0.71	0.83	1.04	1.16	1.28
Ratio V/Fe	1.3	1.3	1.3	1.4	1.4	1.3	1.5
Ratio V/Ni	3.3	3.2	2.9	3.1	4.3	4.0	3.5

Example 5

This example show that iron has little or no effect on catalyst performance. The data is taken from commercial operation on an RCC residual crude processing unit, during a period when iron level on catalyst is at 10,330 ppm as a result of processing high iron contaminated crude. In a similar run, iron level is maintained at 7200-7500 ppm. For both of these periods, nickel and vanadium content are quite similar. Comparison of runs made at low and high iron levels, each over a period of two weeks is shown in Table 5. The results show

that even though there is about 3000 ppm more iron on the high iron catalyst during the high iron two week period, there is little change in conversion or gasoline efficiency and the yields of all products compare very closely. The resultant coke make (wt. % coke - Ramsbottom Carbon) = 5.2 wt. % and 5.8 wt. % respectively for the two weekly low iron runs, and 5.2 wt. % and 5.0 wt. % for the two high iron runs. This shows that the additional iron does not cause an increase in coke make. H₂ is up slightly, increasing about 3.562 liters/liter (20 SCF/bbl.) for the higher metal catalyst. However, nickel, a notorious hydrogen producer and vanadium, a less active hydrogen producer, are both up (approximately 300 to 500 ppm nickel and 600 ppm vanadium). Contrary to conventional wisdom, this data shows that adding large amounts of iron to the catalyst is not detrimental to catalyst activity or yield of valuable products (selectivity). Therefore, intentionally adding iron in order to increase iron content, and thereby enhance magnetic beneficiation, is shown to be technically sound. Note also that even the expensive virgin catalysts used in commercial hydrocarbon conversion operations start out with natural iron levels of 3000 to 4500 ppm (kaolin clay component) and further confirms that iron is not considered harmful even in expensive sophisticated fresh conversion catalysts.

TABLE 5

		IRON PPM			
Iron Content	72-7500 ppm 2 week period	10330-10930 ppm 2 week period			
RCC DATA					
DATE (A)	Week #1	Week #2	Week #3	Week #4	
	Avg.		Avg.		
TOTAL CHG. m ³ /day	5161.1	5072.1	6062.7	5951.4	
(B/D)	(32460)	(31900)	(38130)	(37430)	
Conversion Total	67.4	68.8	68.1	68.2	69.0
Gasol. Efficiency	73.5	73.1	73.3	69.8	72.9
Yields:Dry Gas wt%	3.7	4.0	3.8	3.7	3.8
DRY GAS-FOE vol%	4.0	4.1	4.1	4.1	4.2
C3-C4 vol%	22.9	23.0	23.0	24.7	22.7
C5-430 EP vol%	49.6	50.3	49.9	47.6	50.3
430-630 EP vol%	18.8	17.0	17.9	19.7	19.2
630+SLURRY vol%	13.8	14.2	14.0	12.1	11.7

	COKE wt%	9.3	9.7	9.5	8.7	8.7	8.7
5	H ₂ liter/liter	12.8	13.4		17.1	16.9	
	(scf/bbl)	(72)	(75)		(96)	(95)	
	RX TEMP (°C)	523.9	523.9		521.7	521.7	
	(deg F)	(975)	(975)		(971)	(971)	
	FEED to RISER °C	137.8	131.1		153.3	156.1	
10	(deg F)	(280)	(268)		(308)	(313)	
	REGEN BED °C	722.8	722.8		421.7	721.1	
	(deg. F)	(1333)	(1332)		(1331)	(1330)	
	CAT/OIL RATIO #/#	7.5	7.5		8.2	8.3	
	Delta Coke-Wt%	1.24	1.29		1.07	1.05	
15	SULFUR wt%	2.2	2.6		2.1	2.1	
	UOPK	11.5	11.4		12.0	11.7	
	RBC wt%	4.1	3.9	4.0	3.5	3.7	3.6
	<343.3°C (<650 deg F)	—	—		—	—	
	CAT ANALYSES						
20	Fe ppm	7500	7200		10930	10330	
	Ni ppm	1330	1500		1870	1870	
	V ppm	3630	3670		4270	4230	
	Feed N, ppm	5	6		6	NA	
	Feed V, ppm	6	8		16	NA	

Example 6

In this example, Table 6, commercial runs are both of approximately 5882 m³ (37000 barrel) per day on a mixture of vacuum bottoms, reduced crude, lube oil extract, vacuum tower heavy gas oil and bulk distillate and are made in consecutive weeks with iron rising 830 ppm in one week (from 9500 to 10330 ppm) and nickel and vanadium increasing only slightly. The results show that conversion and gasoline efficiency are essentially unchanged, with gasoline yield actually even slightly higher at the higher metal level. Coke make (coke wt. % - RB carbon wt. %) was 5.0 wt. % for the higher iron catalyst, and was desirably lower than the 5.4 wt. % for the lower iron level catalyst, thus again showing that an increase in iron is not harmful. H₂ increased, only 1.247 liter/liter (7 CF/bbl.) an amount well within experimental error.

TABLE 6

RCC DATA		6A		6B	
Run		Higher Iron		Lower Iron	
5	TOTAL CHG. m ³ /day (B/D)	5951.4	(37430)	5886.2	(37020)
	WOLF Feed	57.24	(360)	87.45	(550)
10	VAC BTMS	712.32	(4480)	683.7	(4300)
	Reduced Crude	1760.13	(11070)	1844.4	(11600)
	No. 4 Vac Btms	0	(0)	0	(0)
	Lube Plt Extract	607.48	(3820)	553.32	(3480)
	LVT HVGO	1038.3	(6530)	992.16	(6240)
15	Bulk Dist.	1776.03	(11170)	1725.15	(10850)
	Trtd Fd-From MRS	0	(0)	0	(0)
	Conversion-Total		69.9		69.4
	Gas. Efficiency		75.9		75.8
	Yields: Dry Gas .-wt%		3.9		3.8
20	DRY GAS-FOE vol%		4.3		4.0
	C3-C4 vol%		20.6		19.9
	C5-430 EP vol%		53.0		52.6
	430-630 EP vol%		18.8		20.2
	630+SLURRY vol%		11.4		10.4
25	COKE wt%		8.7		9.5
	VOLUME GAIN %		+3.7		+3.1
	H2 liter/liter (scf/bbl)	16.92	(95)	15.67	(88)
	H2/Cl RATIO		0.98		0.91
	RX TEMP °C (deg F)	521.7	(971)	521.7	(971)
30	FEED to RISER °C (deg F)	156.1	(313)	156.7	(314)
	REGEN BED °C (deg F)	721.11	(1330)	722.2	(1332)
	CO2/CO RATIO		6.5		6.5
	CAT/OIL RATIO #/#		8.3		8.2
	Delta Coke -wt%		1.05		1.16
35	FEED GRAV-deg API		21.0		20.4
	SULFUR wt%		2.1		2.3
	UOPK		11.7		11.5
	RBC wt%		3.7		4.1
	<343.3°C (<650 deg F)		--		--
40	CAT ANALYSES				
	Fe ppm		10330		9500
	Ni ppm		1870		1750
	V ppm		4230		3950
	SA m2/g		114		121
45	Pv cm ³ /g		0.29		0.28

Example 7

50 In another experiment, 80 grams of reddish appearing (iron contaminated) equilibrium catalyst containing iron, nickel and vanadium having a similar iron content (11,600 ppm) as used in the previous example, is mixed thoroughly with 20 g of grayish white colored virgin FOC-90 (Filtrol Corp.) catalyst, containing approximately 4,000 ppm of iron and essentially no nickel. The mixture is subjected to magnetic separation by processing over a rare earth roller magnetic separator, with a steel belt (to eliminate or reduce electrostatic charge which

55 interferes with magnetic separation) 0.0079 cm (0.00311 thick) 15.24 cm (6") wide, at a speed of 45.7 m/minute (150 fpm feet/minute), and 0.89 kg/hr/cm (5 lb/hr/in) of belt width with a splitter placed to properly catch the two fractions. Two portions, (1) 19.8 g of absolutely clean grayish white virgin catalyst, and (2) 80.2 g of reddish high iron catalyst were recovered from the mixture after magnetic processing. This shows the effectiveness of the magnetic separation method. Table 7 shows the composition of both fractions before mixing,

and after separation, and strikingly demonstrates how a high concentration of iron in old catalyst can almost completely achieve magnetic separation from new fresh catalyst for recycle and rejection of old catalyst for disposal. This experiment ideally illustrates how effective magnetic beneficiation can be.

This experiment not only demonstrates how efficient magnetic separation can be (1% loss of virgin catalyst) but also how clean the separation can be. It is apparent that the composition of the two fractions remain essentially the same as before blending, confirming an absence of cross carryover. Comparison of the color of the two ingredients before mixing and after separation also showed them to be identical, a dramatic demonstration of the effectiveness of magnetic separation.

TABLE 7

SEPARATION OF BLENDED VIRGIN AND EQUILIBRIUM REDUCED CRUDE CATALYST

1. Blended mixture of 20 wt.% FOC-90, 80 wt.% Equilibrium RCC Catalyst analyses of each catalyst. Pre mixture chemical analyses

	Fe ppm	Ni ppm	V ppm	
Virgin FOC-90		4,800	300	<100
Equil. RCC Cat		11,200	1,900	4,300

2. Recovery -- Recovered fractions-- Chemical Analysis

	Fe ppm	Ni ppm	V ppm
19.8 wt.% NM portion (FOC-90)	4,900	300	<100
80.2 wt.% M portion (RCC Cat)	11,600	1,900	4,100

Example 4

In ARTCAT[®] sorbent, Example 4, analyses of the products from splitting equilibrium catalyst by magnetic separation into six equal cuts show also how iron and vanadium maintain a close and constant relationship. Normally vanadium, if not immobilized, will spread rapidly from old catalyst particles to new catalyst particles, thereby rapidly shifting the relationship of vanadium to iron, as well as nickel. Therefore, the ratio V/Ni in the low magnetic, low nickel cuts should be high relative to Ni in the high nickel, high magnetic cuts. However, Figure 7 portrays the analytical comparison of the various magnetic cuts of ARTCAT loaded with nickel, iron and vanadium. The data in Table 4, as well as the following Figure 7 show how closely iron and vanadium track each other in a 1.3/1 ratio, thus also demonstrating iron's ability to immobilize vanadia under optimized operating conditions. Note also in Table 4 that the ratio of vanadium to nickel is lower on fresher and lower metal containing catalysts, and higher on old catalyst. This therefore, suggests that iron tends to immobilize vanadium as otherwise, as mentioned above mobile vanadium from older catalyst particles would tend to transfer to lower nickel containing newer catalyst and thus increase the vanadium to nickel ratio as it does in Tables 2 and 3 on RCC catalyst where the iron level and more importantly the incremental iron level (iron in equilibrium catalyst minus iron in virgin catalyst) is much lower than in the ARTCAT[®] sorbent.

Evidence obtained on spent RCC (Table 8) by Electron Spectroscopy Chemical Analysis (ESCA) analysis shows that vanadium can be maintained in a non-mobile form either by immobilization with iron or by keeping it in a reduced plus four state by keeping a small amount of carbon on regenerated particulate. This plus four state is less detrimental to the molecular sieves on which most conversion catalysts are based. Iron's ability

to immobilize vanadium, while at the same time enhancing separation, provides another way of controlling vanadium and adds another unexpected benefit to use of iron.

TABLE 8
EQUILIBRIUM RCC CATALYST
VANADIUM VALENCE ANALYSIS BY ESCA

	RCC Catalyst	Relative Amounts*		
		V ⁺³	V ⁺⁴	V ⁺⁵
15	1. Spent-as received 1.04% coke	1	5	1
	2. Commercial regeneration 0.2% coke	2	4	2
	3. #1-reduced in H ₂ 385°C 1 hour			
	5.066 X 10 ⁶ dynes/m ² (5 atm)	2	6	2
20	4. #1-lab regenerated in air			
	648.9°C (1200°F) 4 hours	1	2	5
	5. #4-lab regenerated plus H ₂			
	385°C 1 hour			
25	5.066 X 10 ⁶ dynes/m ² (5 atm)	1	10	1

*This data shows the relative (V⁺³, V⁺⁴, V⁺⁵) amount of each vanadium valence, as determined by comparing the relative areas under specific and

characteristic vanadium valence peaks as measured by ESCA analysis.

The above results show that in operation, vanadium if maintained in a slightly reduced state (0.2% coke on regenerated RCC Catalyst) tends to exist in the plus four valence state, and as the data shows, is retarded in redispersing from one catalyst particle to another.

In studying magnetic separation on ARTCAT (Figure 2, Table 4), iron and vanadium are closely paired suggesting iron is forming a ferrous compound with four valence vanadium. Vanadium having a plus four valence may form an immobilizing compound with iron, probably Fe⁺² because of the reducing environment. Hence, the combination of adding iron and keeping a small amount of coke on regenerated catalyst, may also be especially effective in controlling vanadium. In effect, the addition of iron not only assists in magnetic separation, but simultaneously may serve to control the zeolite destructive properties of vanadium in cracking catalysts.

Example 9

In the past when operating on gas oil in the praiser, prezeolite cracking era, iron was always considered an undesirable poison, along with nickel, vanadium, and copper. Today, using the latest hydrocarbon conversion technology, including a much more active zeolite promoted and stable catalyst, lift gas and a very short contact time riser reactor, catalytic cracking of carbo-metallic feedstocks appears not to be substantially hurt by iron. Taking the results of 116 weight balance tests on a reduced crude converter over a six year period and plotting selectivity, hydrogen, and coke make versus iron content, and making a regression analysis of all data shows that selectivity (yield of gasoline - divided by conversion remains at 74% with iron ranging between 6,000 to 11,000 ppm as shown in Figure 5. Hydrogen make, a sensitive measure of contamination, also remains constant at 0.15 wt. % between 6,000 and 10,000 ppm and actually decreases slightly at 11,000 ppm (see Figure 6). Coke make, which is also considered a sensitive measure of metal poisoning, actually decreases

es from approximately 10.7 wt. % at 6,000 to 9% at 11,000 ppm (see Figure 4). These weight balances are performed over a six-year period and include runs on a variety of residual feedstocks varying widely in metal content and Ramsbottom Carbon. The data confirm that iron is not harmful, and therefore can be used successfully in enhancing magnetic beneficiation.

Example 10

Magnetic susceptibility measurements can be made on catalyst containing varying amounts of iron and nickel and including iron on virgin catalyst. Figure 8 shows that a plot of incremental magnetic susceptibility in electromagnetic units can be plotted as a direct relationship between incremental iron, plus nickel. When the data is broken down into the contribution of nickel and iron (note the change in slope for three different catalysts, with varying amounts of nickel and iron in Figure 8) as determined by a plot of atomic fraction of each, it shows that iron has a susceptibility value of 225×10^{-6} emu's at 100% iron, and nickel has a magnetic susceptibility of 42×10^{-6} emu's at 100% nickel. Here again iron shows to be much more effective, and in this case is 5-6 times as effective as nickel in effecting beneficiation. This further confirms the effectiveness of the process.

Modifications

Specific compositions, methods, or embodiments discussed are intended to be only illustrative of the invention disclosed by this specification. Variation on these compositions, methods, or embodiments are readily apparent to a person of skill in the art based upon the teachings of this specification and are therefore intended to be included as part of the inventions disclosed herein.

Reference to documents made in the specification is intended to result in such patents or literature being expressly incorporated herein by reference including any patents or other literature references cited within such documents.

Claims

1. A process for processing organic feedstocks by contacting said feedstock with catalytic and/or non-catalytic particles in a fluid bed conversion system, said process comprising in combination:
 - (a) adding to said conversion system a magnetically active moiety so it deposits on the particles over a period of time so that deposition of said moiety on said particles is proportional to the time that said particles have remained in the system; and
 - (b) separating older particles added early to the system from newer particles later added, by magnetic means.
2. A process according to Claim 1 wherein said organic feedstocks comprise vanadium, nickel or other contaminating metals.
3. A process as claimed in Claim 1, wherein said moiety comprises an iron compound which is added continuously, cyclically or periodically to the feedstock so as to deposit on the particulate in amounts in the range of about 0.1 to 10 ppm of iron to one part of nickel equivalents.
4. A process as claimed in Claim 1, wherein said moiety comprises an iron compound which is added continuously or periodically to the feedstock so as to deposit on the particulate in amounts in the range of about 0.5 to 2 ppm of iron to one part of nickel equivalents, and wherein said organic feedstock comprises metal contaminants which deposit on said particles.
5. A process as claimed in Claim 3, wherein said iron compound is added as an inorganic iron compound, as an organic iron compound, as a water soluble iron compound, which is emulsified in oil and added to an additive, as an oil soluble iron compound.
6. A process as claimed in Claim 3, wherein said iron compound is added in an organic solvent to a residual feedstock.
7. A process as claimed in Claim 1, wherein catalyst particles containing higher amounts of magnetically active ions or element also contain higher levels of nickel equivalents of contaminating metals and are

separated by magnetic separation from catalyst particles containing lower amounts of magnetically active ions or elements and also lower levels of nickel equivalents.

- 5 8. A process as claimed in Claim 1, wherein the magnetic means comprises a high gradient electromagnetic separation device having about 1,000 to to 20,000 Gauss field strength.
9. A process as claimed in Claim 1, wherein the magnetic means comprises a magnetic roller.
- 10 10. A process as claimed in Claim 1, wherein the magnetic means comprises a superconducting high gradient electro magnetic separator (SCHGMS) wherein the SCHGMS operates in the range of about 10,000 to 50,000 Gauss magnetic field strength .
11. A process as claimed in Claim 1, wherein the feedstock has a Conradson Carbon number greater than 1, and wherein the feedstock has an API gravity between 10 and 30, and wherein the particles have a
15 nickel equivalent, excluding iron, of 500 ppm or greater.
12. A process as claimed in Claim 3, wherein said iron is added as ferrous or ferric sulfate.
13. A process as claimed in Claim 3, wherein iron is added as a water soluble salt, or as an oil soluble com-
20 pound, as an organic compound, or as an emulsion.
14. A process as claimed in Claim 1, wherein a magnetically active moiety, which does not substantially re-
duce catalyst selectivity or activity, is added at a rate proportional to the metal contaminants in the feed-
stock.
- 25 15. A process as claimed in Claim 3, wherein said iron compound is added to the feedstock or to the catalyst or particulate at a rate 0.5 to 2 times the moles of vanadium contaminant in the feedstock, so as to form an iron vanadate.
- 30 16. A process according to Claim 1, wherein the magnetic separation occurs at a particulate temperature of from about -100°F to 400°F (-55 to 205°C).
17. A process as claimed in Claim 1, whereby iron as an iron compound, manganese or rare earth compound is added continuously to the catalyst by means of a solution sprayed directly on the circulating catalyst.
- 35 18. A process as claimed in Claim 1, whereby said magnetic means comprises a non-magnetic stainless steel, or other electrostatic eliminating, endless belt.
19. A process according to claim 1 wherein the magnetically active moiety comprises a manganese com-
40 pound.
20. A process according to claim 1 wherein the magnetically active moiety comprises a chromium compound.
21. A process according to claim 1 wherein the magnetically active moiety comprises a manganese, iron or
rare earth compound which has a magnetic susceptibility of at least 500×10^{-6} CGS per gram formula
45 (or atomic) weight at 293°K.
22. A process according to claim 1 wherein the magnetically active moiety comprises a manganese, iron or
rare earth compound which has a susceptibility of at least 3500×10^{-6} CGS per gram formula weight.
- 50 23. A process according to claim 1 wherein said moiety comprises an iron compound.
24. A process according to claim 1 wherein said moiety comprises a heavy rare earth.
25. A process according to Claim 1 for reducing molecular weight by cracking gas oil or heavier hydrocarbon
fractions in a conversion system in the presence of recycled circulating catalytic cracking catalyst par-
55 ticles, said process comprising in combination:
A. intentionally adding an iron compound, a manganese compound or a rare earth compound to said
circulating catalyst particles so that the concentration of iron, manganese or a rare-earth element on
a particle increases in magnetic susceptibility proportional to the time that the catalyst particle has
remained in the system,

B. separating old catalyst earlier added to the system and high in iron, manganese or rare earth content, from catalyst more recently added, by magnetic separation.

5

Patentansprüche

1. Verfahren zur Behandlung von organischem Beschickungsmaterial durch Inkontaktbringen des Beschickungsmaterials mit katalytischen und/oder nicht-katalytischen Teilchen in einem Umwandlungssystem mit Fließbett, dadurch **gekennzeichnet**, daß das Verfahren kombiniert
10 (a) die Zugabe einer magnetisch aktiven Komponente zu dem Umwandlungssystem, so daß sich diese auf den Teilchen im Verlauf einer Zeit absetzt, so daß die Abscheidung der Komponente auf den Teilchen proportional zu der Zeit ist, die die Teilchen in dem System verblieben sind; und
15 (b) die Abtrennung älterer Teilchen, die früh zu dem System zugegeben worden sind, von neueren Teilchen, die später zugegeben worden sind, mittels magnetischer Maßnahmen umfaßt.
2. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß das organische Beschickungsmaterial Vanadium, Nickel oder andere Verunreinigungsmetalle umfaßt.
- 20 3. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die Komponente eine Eisenverbindung, welche kontinuierlich, zyklisch oder periodisch zu dem Beschickungsmaterial zugegeben wird, so daß sie sich auf den feinen Teilchen in Mengen im Bereich von etwa 0,1 bis 10 ppm Eisen, bezogen auf einen Teil Nickel-Äquivalente, abscheidet, umfaßt.
- 25 4. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die Komponente eine Eisenverbindung, die kontinuierlich oder periodisch zu dem Beschickungsmaterial zugegeben wird, so daß sie sich auf den feinen Teilchen in Mengen im Bereich von etwa 0,5 bis 2 ppm Eisen, bezogen auf einen Teil Nickel-Äquivalente, abscheidet, umfaßt, und wobei das organische Beschickungsmaterial Metallverunreinigungen enthält, die sich auf den Teilchen abscheiden.
- 30 5. Verfahren nach Anspruch 3, dadurch **gekennzeichnet**, daß die Eisenverbindung als anorganische Eisenverbindung, als organische Eisenverbindung, als wasserlösliche Eisenverbindung, die in Öl emulgiert und zu einem Additiv zugegeben wird, als Öl-lösliche Eisenverbindung zugegeben wird.
- 35 6. Verfahren nach Anspruch 3, dadurch **gekennzeichnet**, daß die Eisenverbindung in einem organischen Lösungsmittel zu einem Rest Beschickungsmaterial zugegeben wird.
7. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die Katalysatorteilchen, welche höhere Mengen an magnetisch aktiven Ionen oder Elementen enthalten, ebenfalls höhere Mengen an Nickel-Äquivalenten von Verunreinigungsmetallen enthalten, und durch magnetische Trennung von den Katalysatorteilchen, welche niedrigere Mengen an magnetisch aktiven Ionen oder Elementen und ebenfalls niedrigere Mengen an Nickel-Äquivalenten enthalten, abgetrennt werden.
- 40 8. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetischen Maßnahmen eine elektromagnetische Trennvorrichtung mit einer Feldstärke von etwa 1000 bis 20000 Gauss mit hohem Gradienten umfassen.
- 45 9. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetischen Maßnahmen eine magnetische Walze umfassen.
- 50 10. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetischen Maßnahmen einen elektrischen, superleitenden, magnetischen Separator mit hohem Gradienten (SCHGMS) umfassen, wobei der SCHGMS im Bereich von etwa 10000 bis 50000 Gauss magnetischer Feldstärke arbeitet.
- 55 11. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß das Beschickungsmaterial eine Conradson-Kohlenstoffzahl über 1 besitzt, und daß das Beschickungsmaterial eine API-Schwere zwischen 10 und 30 besitzt, und daß die Teilchen ein Nickel-Äquivalent, ausgenommen Eisen, von 500 ppm oder darüber besitzen.

12. Verfahren nach Anspruch 3, dadurch **gekennzeichnet**, daß das Eisen als Eisen(II)- oder Eisen(III)-sulfat zugegeben wird.
- 5 13. Verfahren nach Anspruch 3, dadurch **gekennzeichnet**, daß das Eisen als wasserlösliches Salz oder als Öl-lösliche Verbindung, als organische Verbindung oder als Emulsion zugegeben wird.
14. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetisch aktive Komponente, die im wesentlichen die Katalysatorselektivität oder -aktivität nicht verringert, in einer Menge proportional zu
10 den Metallverunreinigungen in dem Beschickungsmaterial zugegeben wird.
15. Verfahren nach Anspruch 3, dadurch **gekennzeichnet**, daß die Eisenverbindung zu dem Beschickungs-
material oder zu dem Katalysator oder zu den feinen Teilchen in einer Menge vom 0,5 bis 2fachen, bezo-
gen auf die Mole der Vanadiumverunreinigung, in dem Beschickungsmaterial zugegeben wird, so daß ein
15 Eisenvanadat gebildet wird.
16. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetische Trennung bei einer Tempe-
ratur der feinen Teilchen von -100°F bis 400°F (-55 bis 205°C) erfolgt.
- 20 17. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß Eisen als eine Eisenverbindung, eine Man-
ganverbindung oder eine Verbindung eines Metalls der seltenen Erden kontinuierlich zu dem Katalysator
als Lösung, die direkt auf den zirkulierenden Katalysator gesprüht wird, zugegeben wird.
18. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetischen Maßnahmen ein nicht-
magnetisches rostfreies Stahlband oder ein anderes endloses elektrostatisches Eliminationsband um-
25 fassen.
19. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetisch aktive Komponente eine Man-
ganverbindung umfaßt.
- 30 20. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetisch aktive Komponente eine
Chromverbindung umfaßt.
21. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetisch aktive Komponente eine Ver-
bindung von Mangan, Eisen oder einem Metall der seltenen Erden umfaßt, welche eine magnetische Sus-
zeptibilität von mindestens 500×10^{-6} CGS pro Gramm Formel- (oder Atom-) Gewicht bei 293°K besitzt.
35
22. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die magnetisch aktive Komponente eine Ver-
bindung von Mangan, Eisen oder einem Metall der seltenen Erden umfaßt, die eine Suszeptibilität von
mindestens 3500×10^{-6} CGS pro Gramm Formel-Gewicht besitzt.
- 40 23. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die Komponente eine Eisenverbindung um-
faßt.
24. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die Komponente ein Metall der schweren Er-
den umfaßt.
45
25. Verfahren nach Anspruch 1 für die Verringerung des Molekulargewichts durch Cracken von Gasöl oder
schwereren Kohlenwasserstoff-Fractionen in einem Umwandlungssystem in Anwesenheit von
rezyklierten, zirkulierenden, katalytischen Crack-Katalysatorteilchen, dadurch **gekennzeichnet**, daß
das Verfahren in Kombination umfaßt:
50 A. die gewollte Zugabe einer Eisenverbindung, einer Manganverbindung oder einer Verbindung eines
Metalls der seltenen Erden zu den zirkulierenden Katalysatorteilchen, so daß sich die Konzentration
an Eisen, Mangan oder Element der seltenen Erden auf den Teilchen, ausgedrückt als magnetische
Suszeptibilität, proportional zu der Zeit, die die Katalysatorteilchen in dem System verbleiben, erhöht,
B. Abtrennung des alten Katalysators, der früher zu dem System zugegeben worden ist, und eines ho-
hen Eisen-, Mangan- oder seltenen Erden-Gehalts von dem Katalysator, der später zugegeben worden
55 ist, durch magnetische Abtrennung.

Revendications

- 5 1. Un procédé pour traiter des réserves organiques en mettant en contact ladite réserve avec des particules catalytiques et/ou non catalytiques dans un système de conversion à lit fluidisé, ledit procédé comprenant en combinaison les étapes consistant :
 - (a) à ajouter audit système de conversion une fraction magnétiquement active, se déposant ainsi sur les particules pendant une certaine durée de sorte que le dépôt de ladite fraction sur lesdites particules est proportionnel à la durée que lesdites particules sont restées dans le système ; et
 - 10 (b) à séparer, à l'aide de moyens magnétiques, les particules plus vieilles ajoutées précédemment au système, des particules plus récentes ajoutées en dernier.
- 15 2. Un procédé selon la revendication 1, dans lequel lesdites réserves organiques comprennent du vanadium, du nickel ou d'autres métaux contaminants.
3. Un procédé comme revendiqué à la revendication 1, dans lequel ladite fraction comprend un composé de fer qui est ajouté continuellement, cycliquement ou périodiquement à la réserve afin de se déposer sur les particules en des quantités comprises entre environ 0,1 et 10 ppm de fer pour une partie d'équivalents nickel.
- 20 4. Un procédé comme revendiqué à la revendication 1, dans lequel ladite fraction comprend un composé de fer, qui est ajouté continuellement ou périodiquement à la réserve afin de se déposer sur les particules en quantités comprises entre environ 0,5 et 2 ppm de fer pour une partie d'équivalents nickel, et dans lequel ladite réserve organique comprend des contaminants métalliques qui se déposent sur lesdites particules.
- 25 5. Un procédé comme revendiqué à la revendication 3, dans lequel ledit composé de fer est ajouté sous forme de composé de fer minéral, sous forme de composé de fer organique, sous forme de composé de fer hydrosoluble, qui est émulsifié dans l'huile et ajouté à un additif, sous forme de composé de fer liposoluble.
- 30 6. Un procédé comme revendiqué à la revendication 3, dans lequel ledit composé de fer est ajouté dans un solvant organique à une réserve résiduelle.
- 35 7. Un procédé comme revendiqué à la revendication 1, dans lequel les particules catalytiques contenant des quantités supérieures d'ions ou d'éléments magnétiquement actifs contiennent également des teneurs supérieures d'équivalents nickel de métaux contaminants, et sont séparées par séparation magnétique des particules catalytiques contenant des quantités inférieures d'ions ou d'éléments magnétiquement actifs et également des teneurs inférieures d'équivalents nickel.
- 40 8. Un procédé comme revendiqué à la revendication 1, dans lequel les moyens magnétiques comprennent un dispositif de séparation électromagnétique à gradient élevé ayant une intensité de champ d'environ 1 000 à 20 000 Gauss.
- 45 9. Un procédé comme revendiqué à la revendication 1, dans les moyens magnétiques comprennent un rouleau magnétique.
10. Un procédé comme revendiqué à la revendication 1, dans lequel les moyens magnétiques comprennent un séparateur électromagnétique à gradient élevé supraconducteur (SCHGMS) dans lequel le SCHGMS fonctionne dans la gamme d'intensités de champ magnétique d'environ 10 000 à 50 000 Gauss.
- 50 11. Un procédé comme revendiqué à la revendication 1, dans lequel la réserve présente un indice de résidu Conradson supérieur à 1, et dans lequel la réserve présente une densité API comprise entre 10 et 30, et dans lequel les particules ont un équivalent nickel à l'exclusion du fer, de 500 ppm ou plus.
- 55 12. Un procédé comme revendiqué à la revendication 3, dans lequel ledit fer est ajouté sous forme de sulfate ferreux ou ferrique.
13. Un procédé comme revendiqué à la revendication 3, dans lequel le fer est ajouté sous forme d'un sel hydrosoluble, ou sous forme d'un composé liposoluble, sous forme d'un composé organique ou sous forme d'émulsion.

14. Un procédé comme revendiqué à la revendication 1, dans lequel une fraction magnétiquement active, qui ne réduit pas sensiblement la sélectivité ou l'activité catalytique, est ajoutée à un taux proportionnel aux contaminants métalliques dans la réserve.
15. Un procédé comme revendiqué à la revendication 3, dans lequel ledit composé de fer est ajouté à la réserve, au catalyseur ou aux particules à un taux de 0,5 à 2 fois le nombre de moles de contaminant de vanadium dans la réserve, afin de former un vanadate de fer.
16. Un procédé comme revendiqué à la revendication 1, dans lequel la séparation magnétique se produit à une température des particules d'environ -100°F à 400°F (-55 à 205°C).
17. Un procédé comme revendiqué à la revendication 1, dans lequel le fer, sous forme de composé de fer, de composé de manganèse ou de terres rares, est ajouté en continu au catalyseur au moyen d'une solution pulvérisée directement sur le catalyseur en circulation.
18. Un procédé comme revendiqué à la revendication 1, dans lequel lesdits moyens magnétiques comprennent une courroie sans fin en acier inoxydable non magnétique ou autre, éliminant l'électricité statique.
19. Un procédé selon la revendication 1, dans lequel la fraction magnétiquement active comprend un composé de manganèse.
20. Un procédé selon la revendication 1, dans lequel la fraction magnétiquement active comprend un composé de chrome.
21. Un procédé selon la revendication 1, dans lequel la fraction magnétiquement active comprend un composé de manganèse, de fer ou de terres rares, qui présente une susceptibilité magnétique d'au moins 500×10^{-8} CGS par poids de formule gramme (ou atomique) à 293°K.
22. Un procédé selon la revendication 1, dans lequel la fraction magnétiquement active comprend un composé de manganèse, de fer ou de terres rares, qui présente une susceptibilité d'au moins $3\,500 \times 10^{-8}$ CGS par poids de formule gramme.
23. Un procédé selon la revendication 1, dans lequel ladite fraction comprend un composé de fer.
24. Un procédé selon la revendication 1, dans lequel ladite fraction comprend une terre rare lourde.
25. Un procédé selon la revendication 1 pour réduire la masse moléculaire en craquant des fractions de gas-oil ou d'hydrocarbures plus lourds dans un système de conversion en présence de particules de catalyseur de craquage catalytique en circulation recyclée, ledit procédé comprenant en combinaison les étapes consistant :
 - A. à ajouter intentionnellement un composé de fer, un composé de manganèse ou un composé de terres rares auxdites particules catalytiques en circulation de façon que la concentration du fer, du manganèse ou d'un élément de terres rares sur une particule augmente en susceptibilité magnétique proportionnellement à la durée que la particule catalytique reste dans le système,
 - B. à séparer le vieux catalyseur précédemment ajouté au système et à teneur élevée en fer, en manganèse ou en terres rares, du catalyseur plus récemment ajouté, à base d'une séparation magnétique.

FIG. 1

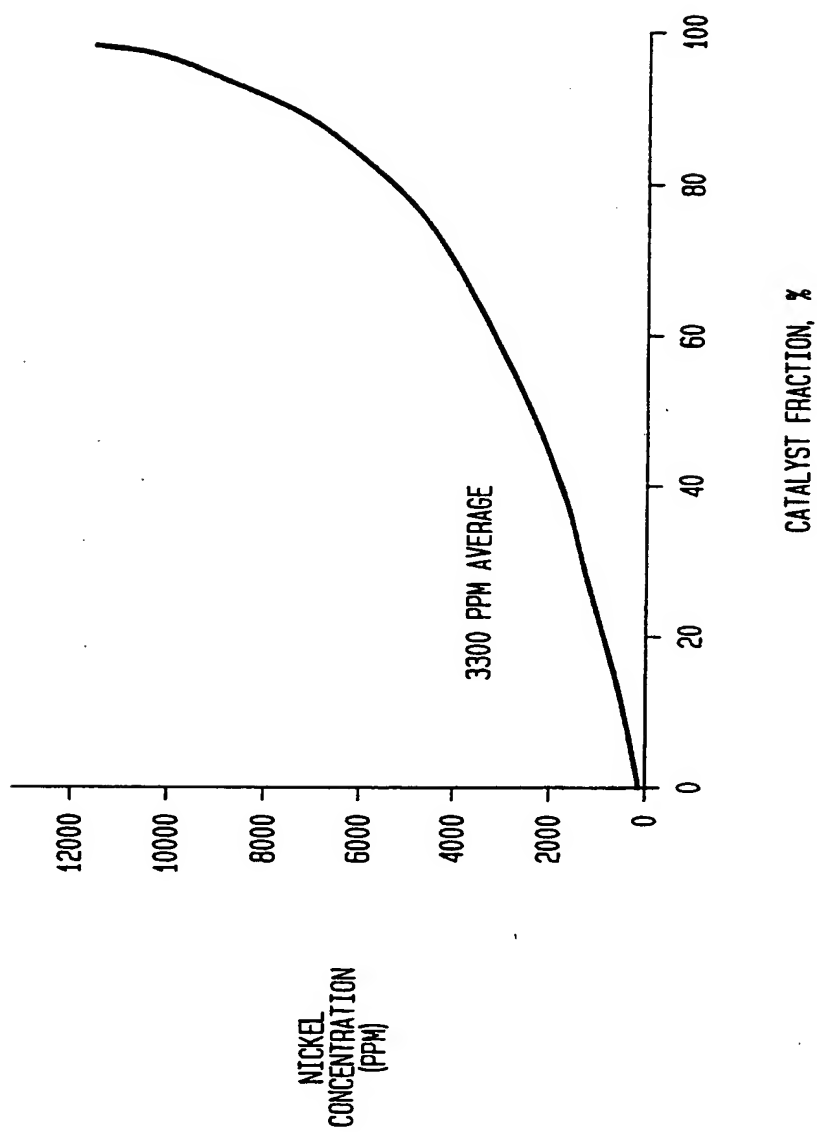


FIG. 2

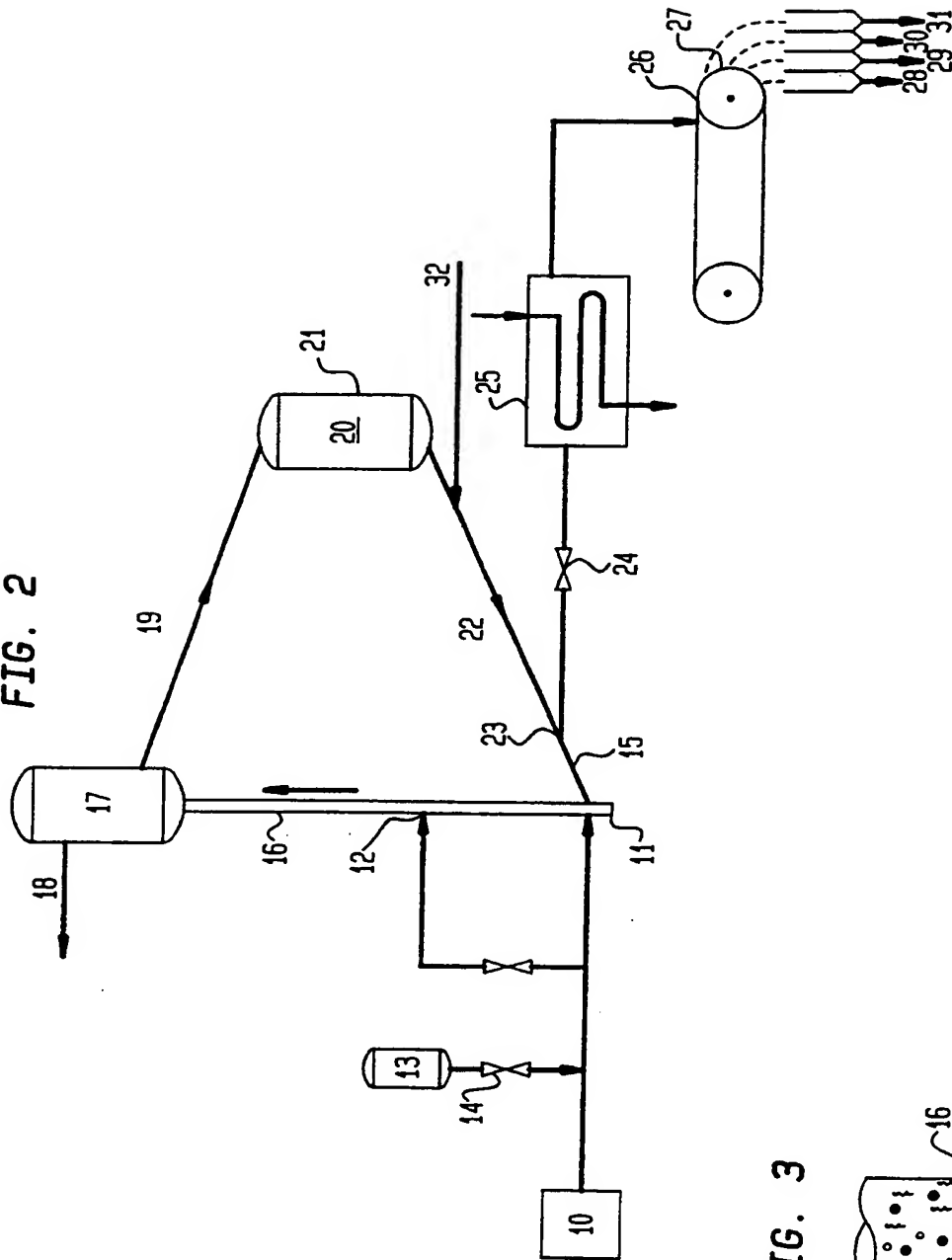


FIG. 3

FIG. 4

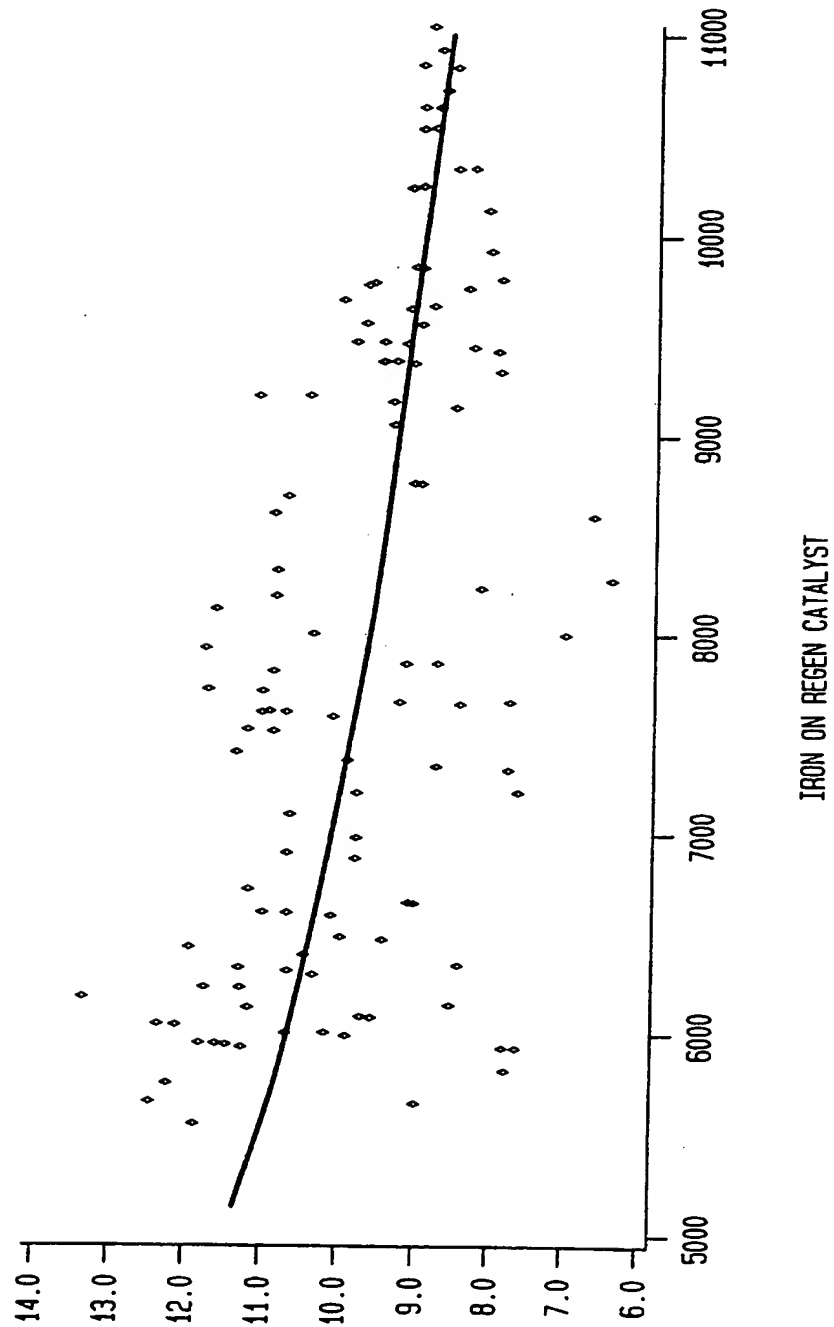


FIG. 5

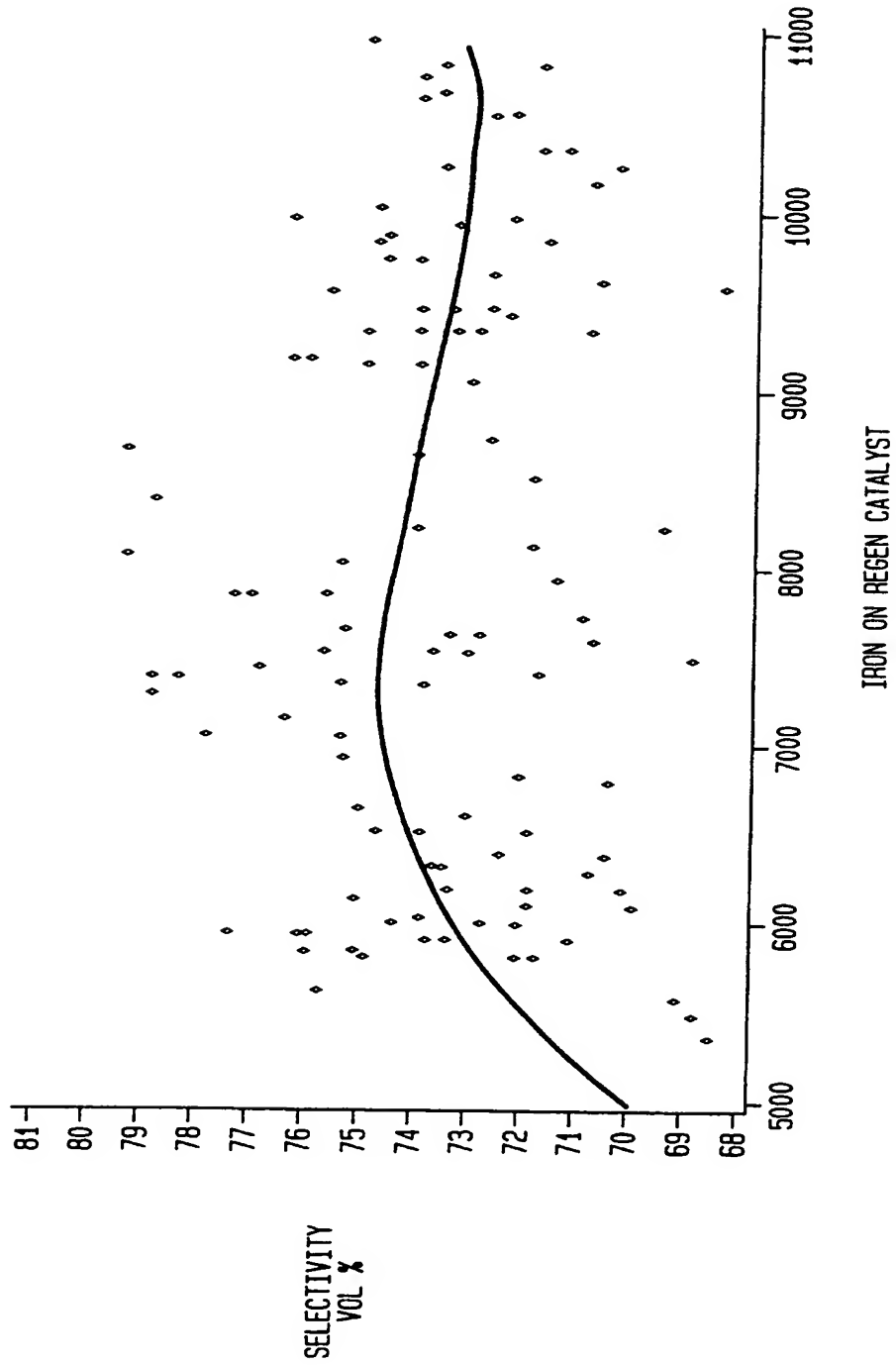


FIG. 6

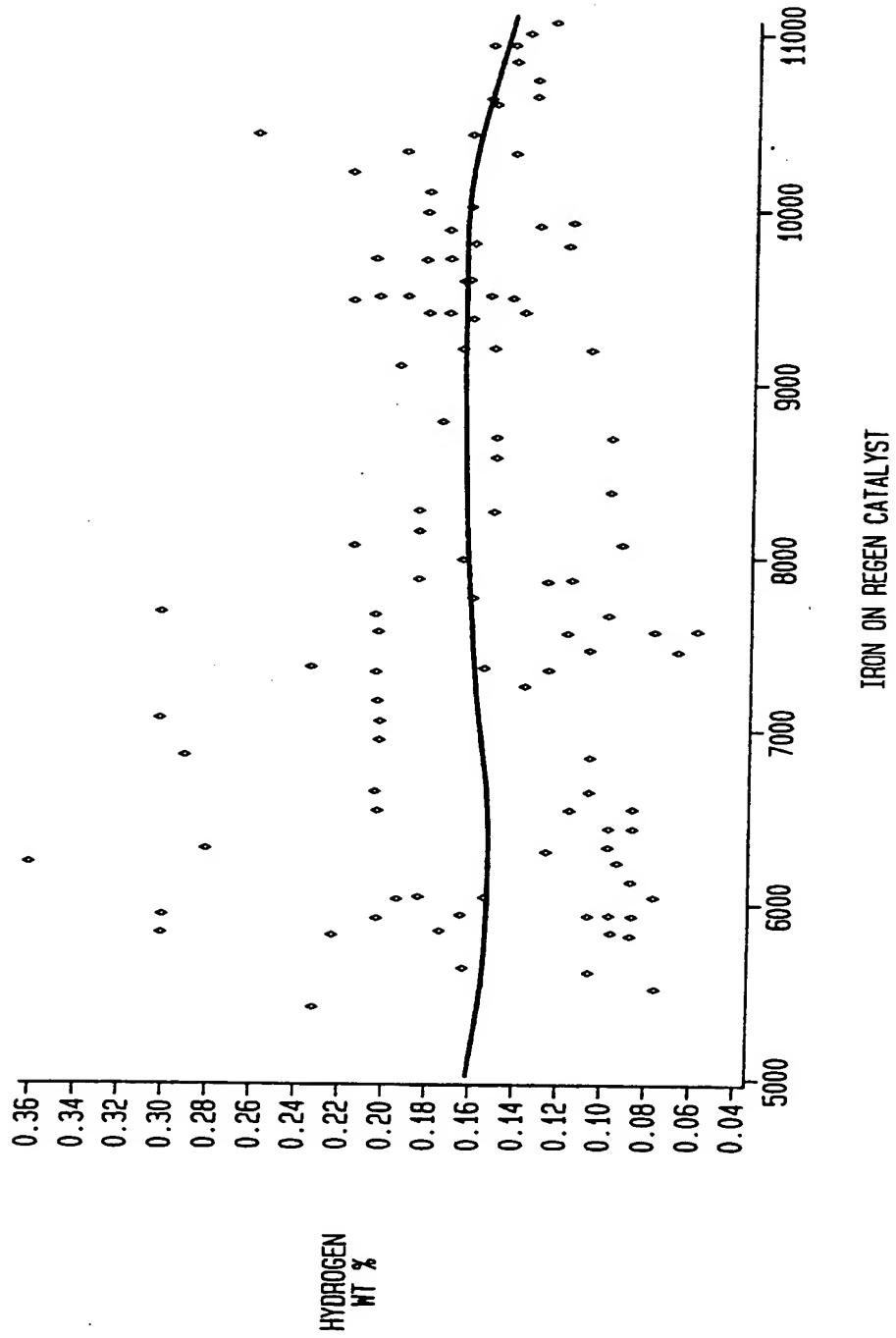


FIG. 7

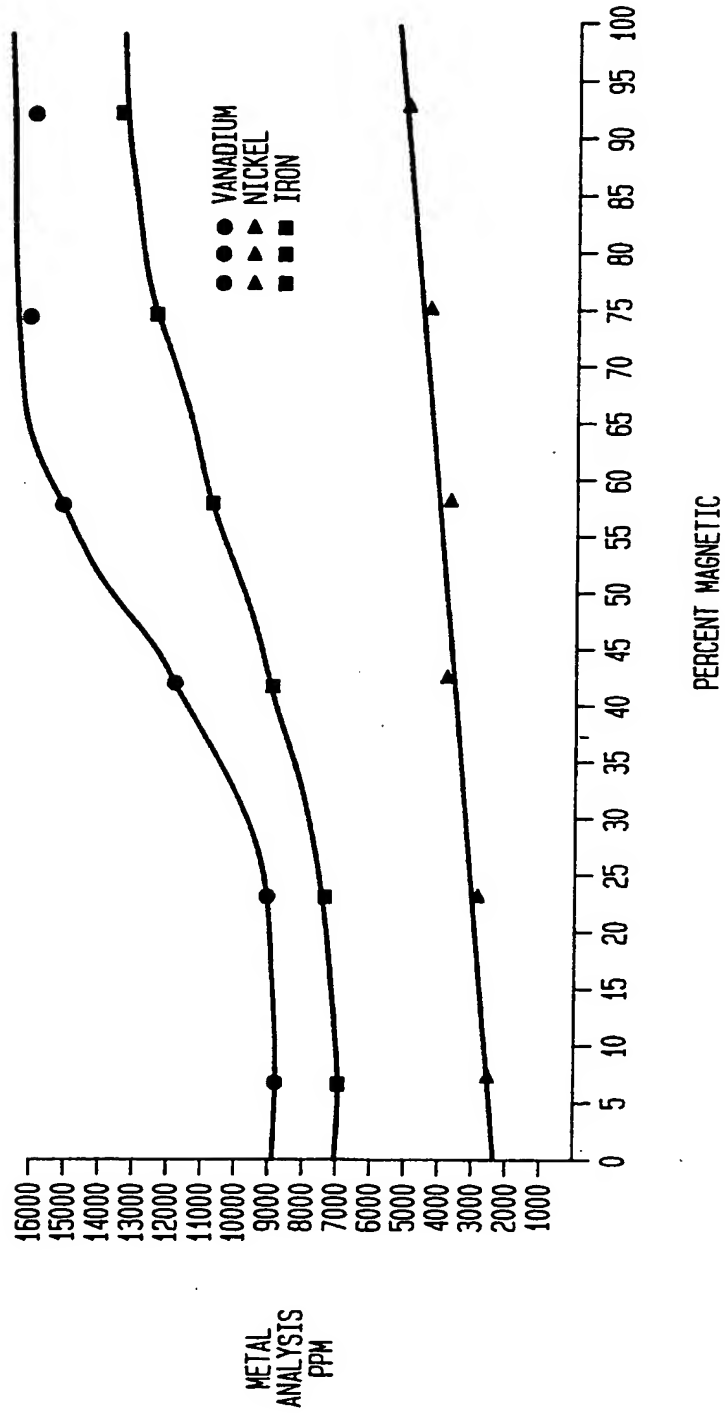




FIG. 8

